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THE INVESTIGATION OF ALKYLMAGNESIUM HYDRIDES

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SUMMARY

The synthesis of alkyl- and arylmagnesium hydrides by a number of different methods in both polar and non polar solvents, has been attempted.

Redistribution of dialkylmagnesium compounds with magnesium hydride to form alkylmagnesium hydrides was attempted using various sources of magnesium hydride. Redistribution failed even when catalytic quantities of triethyl aluminum were added to the reaction vessel.

Hydrogenolysis of unsymmetrical dialkylmagnesium compounds ($RMgR'$) did not produce the expected RMgH compounds. Instead the disproportionation products ($R_2Mg + MgH_2$) were observed. The unsymmetrical dialkylmagnesium compounds studied contained one alkyl group easily removed by hydrogenolysis and one alkyl group difficultly removed by hydrogenolysis. Thus $CH_3Mgs\text{-}C_4H_9$ was expected to produce CH_3MgH on hydrogenolysis rather than $(CH_3)_2Mg$ and MgH_2. However under conditions of partial hydrogenolysis, $RMgR'$ compounds did form a stable alkylmagnesium hydride complexed to an additional molecule of unsymmetrical dialkylmagnesium compound, namely, $RMgH \cdot RMgR'$.

Molecular association and low temperature nmr studies verified the nature of the $RMgH \cdot RMgR'$ complexes in both diethyl ether and benzene solvent.

CHAPTER I

INTRODUCTION

Attempts to synthesize alkylmagnesium hydrides have been very limited even though these compounds are analogs of Grignard reagents which undoubtedly are among the most useful reagents in synthetic organic chemistry. It was the purpose of the present study to investigate some preparative routes to alkyl- and arylmagnesium hydrides and to characterize the resulting products.

Preparation of Dialkylmagnesium Compounds

The dialkylmagnesium reagents used in the present study were prepared by a method developed by C. W. Kamienski.[1] The method involves (1) an exchange reaction involving an alkyllithium reagent with magnesium chloride or an alkylmagnesium halide and (2) redistribution of two different symmetrical dialkylmagnesium compounds to form one unsymmetrical dialkylmagnesium compound.

$$(1)\quad 2\ RLi + MgCl_2 \rightarrow R_2Mg + 2\ LiCl$$

$$(2)\quad R_2Mg + R'_2Mg \rightarrow 2\ RMgR'$$

Kamienski found that exchange reactions of alkyllithium reagents with magnesium chloride are complete and rapid only when the magnesium chloride has been

"activated." Commercially available anhydrous magnesium chloride was found not to be suitable for this reaction. Of several methods Kamienski investigated for synthesizing "activated" magnesium chloride, the most satisfactory one was the reaction of a chloro Grignard reagent with benzyl chloride.

$$(3)\quad RMgCl + C_6H_5CH_2Cl \rightarrow MgCl_2 + C_6H_5CH_2R$$

Kamienski found that a particular crystalline modification of $MgCl_2$ was more reactive in the exchange reaction compared to other modifications. Alkyllithium reagents were also found to react readily with alkylmagnesium chlorides in ethereal media. Yields were reported to be quantitative. The resulting dialkylmagnesium reagents could be desolvated and redissolved in benzene. Grignard reagent and alkyllithium reagent exchange was found to be a particularly easy route for the preparation of unsymmetrical dialkylmagnesium reagents especially when the alkyl lithium reagent used was stable in other solutions, e.g. CH_3Li, C_6H_5Li. Unsymmetrical or mixed dialkylmagnesium compounds have also been formed by simply mixing a hydrocarbon solution of two different dialkylmagnesium compounds.

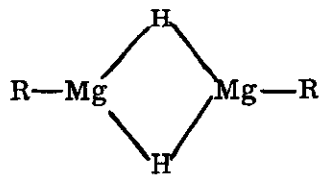
Methods of Preparation of Alkylmagnesium Hydrides

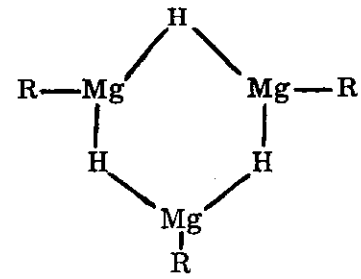
Kamienski[1] found that THF (tetrahydrofuran), TED (triethylenediamine) and TMEDA (tetramethylethylemediamine) stabilize and prevent decomposition of dialkylmagnesium reagents. After extended refluxing at 70°-80°, di-t-butyl and i-sec-butylmagnesium did not eliminate olefin in the presence of these bases.

However, in the absence of bases the t-butyl compound decomposed even at room temperature and the sec-butyl compound pyrolyzed slowly at reflux temperatures of 70^{o}-80^{o}. He proposed an olefin elimination reaction to describe the decomposition; however this was never proven.

$$(4)\quad R_2Mg \xrightarrow{\Delta} RMgH + \text{olefin}$$

Di-sec-butylmagnesium which has undergone partial elimination is able to effect metallation of toluene, even in the presence of a Lewis base. Toluene could not be metallated by a dialkylmagnesium compound in the presence of a base prior to pyrolysis. These observations were explained by partial pyrolysis enhancing the reactivity of dialkylmagnesium compounds by forming a soluble, self-associated form of alkylmagnesium hydride. Tentatively Kamienski proposed the structures below for alkylmagnesium hydrides.





The proposed structures were based on a comparison of the known structures of dialkylaluminum hydrides (R_2AlH), aluminum alkyls (R_3Al), and diborane. In the latter cases sufficient documentation exists to support metal-alkyl and metal-hydrogen bridge systems.

R. Bauer[2] studied the reaction of silane and diethylmagnesium in ether and proposed the following reaction sequence.

$$(5)\quad Mg(C_2H_5)_2 + SiH_4 \rightarrow HMgC_2H_5 + H_3SiC_2H_5$$

$$(6)\quad HMgC_2H_5 + (C_2H_5)_2O \rightarrow HMgOC_2H_5 + C_4H_{10}$$

However, Bauer offered no supporting data to verify the formation of $HMgC_2H_5$.

G. E. Coates, et al,[3] reported that diethylmagnesium and sodium triethylborohydride react to produce diethylmagnesium and magnesium hydride at 0^o in diethyl ether. However, when the reaction was carried out at -78^o, no magnesium hydride precipitated from solution. When a sample of the reaction mixture at -78^o was taken from the reaction flask and hydrolyzed, an ethane:hydrogen ratio of 1:1 was observed. If the original reactants had been present the ethane:hydrogen ratio would have been 1:2. The following reaction was proposed:

$$(7)\quad NaEt_3BH + Et_2Mg \rightleftarrows EtMgH + NaEt_4B$$

(Sodium tetraethylboron is stable even in mildly acidic solutions). Coates reported that ethylmagnesium hydride is stable at -78^o but disproportionates at -20^o causing magnesium hydride to precipitate.

$$(8)\quad 2\ EtMgH \rightleftarrows Et_2Mg + MgH_2$$

The addition of TMEDA to the original reaction mixture prevented the formation of a precipitate; however, no RMgH compound was formed.

Purpose

The purpose of this investigation was to find a suitable method to synthesize alkylmagnesium hydrides and to characterize these compounds.

Approach

The principal synthetic routes studied involved the redistribution of dialkylmagnesium compounds with magnesium hydride and the hydrogenolysis of unsymmetrical dialkylmagnesium compounds.

All synthetic attempts were carried out in both benzene and diethyl ether solvents since the composition of these compounds in both polar and non polar solvents might be different. It was also hoped that if disproportionation took place in diethyl ether, it might not take place in benzene solvent.

The principal tools used in this investigation were high pressure hydrogenation instrumentation, 100 MHz and 60 MHz nmr and infrared spectrometers as well as high vacuum apparatus for gas analysis.

CHAPTER II

EXPERIMENTAL

Apparatus

Instrumentation

A 60 MHz Varian A-60 nmr spectrometer and a 100 MHz Japan Optical and Electron Co., Ltd. nmr spectrometer were used.

Infrared spectra were obtained on a Perkin-Elmer 621 Spectrophotometer.

Inert Atmosphere

Chemical reactions and manipulations were performed under dry nitrogen at the bench or in a nitrogen filled glove box.[4]

Analytical

Halogen analysis was performed by the Volhard method. Magnesium analysis was carried out by titration with EDTA. Lithium and sodium analyses were carried out by flame photometry. Analysis of gaseous hydrocarbons was carried out on a high vacuum line.[4]

Chemicals

Benzyl Chloride

Fischer reagent grade benzyl chloride was distilled under vacuum after drying over calcium chloride.

Alkyl Halides

All alkyl halides were Fischer reagent grade, dried over magnesium sulfate prior to use and then distilled.

Lithium Aluminum Hydride

Lithium aluminum hydride was obtained from Lithium Corporation of America and used without further purification.

Sodium Hydride

Sodium hydride was obtained from Ventron Inc.

Alkyllithium

All alkyllithium compounds were obtained from Lithium Corporation of America.

Diethyl Ether

Diethyl ether was Baker's reagent (anhydrous) and was distilled from lithium aluminum hydride prior to use.

Magnesium Sulfate

Magnesium sulfate was Mallinckrodt Analytical Reagent Grade.

Calcium Chloride

Calcium chloride was Fischer Certified.

Benzene

Fischer Certified thiophene free benzene was distilled from sodium aluminum hydride prior to use.

Triethylaluminum

Triethylaluminum was obtained from Texas Alkyls Inc.

Magnesium

Fischer's Grignard reagent grade magnesium turnings were used.

Redistribution Reactions

Preparation of Di-sec-butylmagnesium

A one molar solution of sec-butylmagnesium chloride in diethyl ether was prepared from sec-butyl chloride and magnesium metal. Analysis of the resulting solution gave the following analysis: $sec\text{-}Bu_{1.01}$, $Mg_{1.00}$, $Cl_{1.14}$. The Grignard reagent was refluxed and benzyl chloride was added in 250 mmolar amounts until one mole had been added. Magnesium chloride precipitated and the precipitate was filtered and washed with benzene. The last trace of ether was removed by co-distillation with benzene. An analysis of the magnesium chloride gave a Mg:Cl ratio of 1.00:1.99. Sec-butyllithium solution in cyclohexane was added at 40^{o} to the magnesium chloride so that the molar ratio of sec-butyllithium to magnesium chloride was 1.00:0.75. The solution was stirred for 24 hours. Lithium chloride precipitated leaving di-sec-butylmagnesium in a mixed solvent of benzene and cyclohexane. The lithium chloride was filtered and the solvent removed in vacuo. Half of the product was redissolved in 500 ml. of diethyl ether and the other half was redissolved in benzene. An nmr of the resulting solution was consistent with the spectrum reported by Kamienski[1] for di-sec-butylmagnesium: a quartet at 8.13τ, a doublet at 8.43τ, a triplet at 8.76τ, and a multiplet at 9.76τ.

Preparation of Magnesium Hydride by Reaction of Lithium Aluminum Hydride and Diethylmagnesium

Fifty ml. of a diethylmagnesium ethereal solution (0.5M) was stirred with

25 ml. of a lithium aluminum hydride ethereal solution (0.5M).

$$(1)\quad 2\ Et_2Mg + LiAlH_4 \rightarrow 2\ MgH_2\downarrow + LiAlEt_4$$

Magnesium hydride precipitated immediately and after the suspension was stirred for a period of 2 hours, the resulting 25 mmoles of magnesium hydride was filtered and washed with diethyl ether.

Reaction of Magnesium Hydride and Di-sec-butylmagnesium in Diethyl Ether

Twenty-five mmoles of magnesium hydride were stirred with an ethereal solution of 25 mmoles of di-sec-butylmagnesium for 24 hours. The mixture was then filtered, the residue washed with diethyl ether and finally dried in vacuo. Analysis of the residue showed only magnesium and hydrogen present in the ratio of 1.00:2.05. Analysis of the solution showed only the presence of butane and magnesium in ratio of 1:98:1.00. Infrared analysis of the residue showed the broad magnesium-hydrogen stretching band from ~800 cm^{-1} to ~540 cm^{-1}. The nmr spectrum of the solution was the same as that of di-sec-butylmagnesium: a quartet at 8.39τ, a doublet at 8.76τ, a triplet at 9.43τ, and a multiplet at 10.57τ.

Reaction of Magnesium Hydride and Di-sec-butylmagnesium in Diethyl Ether using a Catalytic Amount of Triethylaluminum

The reaction above was repeated with the exception that two to three drops of triethylaluminum were added. The residue again showed only the presence of magnesium and hydrogen in ratio of 1.00:2.02. The solution was hydrolyzed and exhibited a butane:magnesium ratio of 2.06:1.00.

Reaction of Magnesium Hydride and Di-sec-butylmagnesium in Benzene Solvent.

Twenty-five mmoles of magnesium hydride that had been washed with benzene was added to 25 mmoles of di-sec-butylmagnesium in benzene solvent. The mixture was stirred over a period of 24 hours. The mixture was then filtered and analyzed. The residue exhibited a Mg:H ratio of 1.00:2.06. The filtrate exhibited a butane:Mg ratio of 1.98:1.00.

Reaction of Magnesium Hydride and Di-sec-butylmagnesium in Benzene Solvent using a Catalytic Amount of Triethylaluminum

The above reaction was repeated with the exception that 2 to 3 drops of triethylaluminum were added to the reaction vessel. The mixture was filtered and the filtrate exhibited a butane:Mg ratio of 2.01:1.00. The residue exhibited a Mg:H ratio of 1.00:1.96.

Magnesium Hydride from the Hydrogenolysis of Di-sec-butylmagnesium in Ether and Benzene Solvents

Fifty ml. of an ethereal solution of di-sec-butylmagnesium (0.5M) was hydrogenolyzed at 3,000 psi and 50^{o} over a period of 8 hours. The solution and precipitate were filtered. Analysis of the solution showed no magnesium present. The residue analysis exhibited a Mg:H ratio of 1.00:2.04.

The hydrogenolysis was repeated exactly as above with 50 ml. of a benzene solution of di-sec-butylmagnesium (0.5M). After filtration the filtrate showed no magnesium present. The residue exhibited a Mg:H ratio of 1.00:2.08. The magnesium hydride produced by the above method was used in the redistribution reactions reported below in place of the magnesium hydride produced from lithium

aluminum hydride and diethylmagnesium reported earlier in this thesis.

Reaction of Magnesium Hydride and Di-sec-butylmagnesium in Diethyl Ether

Twenty-five mmoles of magnesium hydride and 25 mmoles of di-sec-butylmagnesium in an ethereal solution were stirred over a 24 hour period. Filtration and analysis of the filtrate exhibited a butane:Mg ratio of 1.94:1.00. Analysis of the residue exhibited a Mg:H ratio of 1.00:1.94.

Reaction of Magnesium Hydride and Di-sec-butylmagnesium in Diethyl Ether using a Catalytic Amount of Triethylaluminum

The above reaction was repeated with the exception that 2 to 3 drops of triethylaluminum were added to the reaction mixture. After filtration the filtrate exhibited a butane: Mg ratio of 2.01:1.00. The residue exhibited a Mg:H ratio of 1.00:1.98.

Reaction of Magnesium Hydride and Di-sec-butylmagnesium in Benzene Solvent

Twenty-five mmoles of magnesium hydride and 25 mmoles of a benzene solution of di-sec-butylmagnesium were stirred together for a 24 hour period. Filtration of the mixture and subsequent analysis of the filtrate gave a butane: Mg ratio of 1.96:1.00. Analysis of the residue gave a Mg:H ratio of 1.00:2.08.

Reaction of Magnesium Hydride and Di-sec-butylmagnesium in Benzene Solvent using a Catalytic Amount of Triethylaluminum

This reaction was carried out exactly as the above reaction with the exception that 2 to 3 drops of triethylaluminum were added to the reaction vessel. After filtration the residue exhibited a Mg:H ratio of 1.00:1.96. The filtrate exhibited a butane:Mg ratio of 2.06:1.00.

Reaction of Di-sec-butylmagnesium and Lithium Aluminum Hydride in Ethereal Solution

One hundred ml. of an ethereal solution of di-sec-butylmagnesium (0.5M) was desolvated *in vacuo* to give 50 mmoles of the neat reagent. To this neat reagent was added 25 ml of a 0.5M ethereal solution of lithium aluminum hydride (12.5 mmoles). The mixture was stirred over a 24 hour period. The solution remained clear for approximately 2 hours, then a white precipitate began to form. After a 24 hour stirring period the mixture was filtered and analyzed. The residue gave the following Al:Mg:H ratio, 0.05:1.00:1.92. The solution gave the following Li:Al:butane:Mg ratio, 1.00:0.98:8.16:2.05. Infrared analysis of the filtrate showed an absorbance at 522 cm^{-1} and at 1805 cm^{-1}.

Reaction of Di-sec-butylmagnesium and Lithium Aluminum Hydride in Benzene Solvent

Two hundred ml. of a benzene solution of di-sec-butylmagnesium (0.5M) and 0.950 g (25 mmoles) of lithium aluminum hydride were stirred together for a 24 hour period. The mixture was filtered and analyzed. The filtrate gave the following Mg:butane ratio, 1.00:2.01. The residue gave the following Li:Al:H ratio, 1.00:0.98:4.05.

Preparation of Unsymmetrical Dialkyl Magnesium Compounds

Preparation of a Methyl-sec-butylmagnesium

Five hundred ml. of a one molar ethereal sec-butylmagnesium chloride solution was prepared. To this solution was added 396 ml. of a 1.26M ethereal solution of methyllithium. Lithium chloride started precipitating immediately

with the generation of some heat. The mixture was stirred over a 12 hour period, and then filtered. Analysis of the supernatent liquid still showed the presence of lithium. This was expected since lithium chloride is slightly soluble in diethyl ether. The supernatent solution was desolvated at 40° in vacuo over a 12 hour period. Five hundred ml. of benzene was then added to the reaction vessel followed by a two hour stirring period. The solution was then filtered and the supernatent liquid analyzed for lithium. Lithium was found to be absent. Further analysis of the solution gave the following butane:Mg:methane ratio, 1.00:1.00:1.02. Two hundred fifty ml. of the solution was then desolvated at 40° in vacuo over a 24 hour period. The residue was then redissolved in diethyl ether. There were then two solutions of methyl-sec-butylmagnesium; 250 ml. of a 0.5M solution in benzene and a like concentration in diethyl ether. Nmr spectra of the ethereal and benzene solutions were obtained: The benzene solution gave a quartet at 8.43τ, a doublet at 8.80τ, a triplet at 9.47τ, a multiplet at 10.61τ, and a singlet at 11.30τ. The ether solution showed the following absorptions: A quartet at 8.05τ, a doublet at 8.28τ, a triplet at 8.49τ, a multiplet at 9.17τ, and a singlet at 11.30τ.

Preparation of Phenyl-sec-butylmagnesium

Five hundred ml. of a 0.5M ethereal solution of sec-butylchloride was prepared in the usual manner. To this solution was added 380 ml. of a 1.32 M solution of phenyllithium. (Phenyllithium solvent was a mixture consisting of 70 percent benzene and 30 percent diethyl ether.) Lithium chloride started to precipitate immediately and some heat was evolved. The mixture was stirred over a 24 hour period. The solution was then filtered and desolvated at 40° in vacuo.

Five hundred ml. of benzene was then added to the reaction vessel, followed by additional stirring for two hours, and re-filtration. Lithium was found to be absent from solution. Two hundred fifty ml. of the solution was desolvated at 40° in vacuo and redissolved in diethyl ether, giving two solutions of 250 ml. (0.5M); one in a benzene solvent and one in an ether solvent. Nmr spectra indicated a phenyl:sec-butyl ratio of 1:1. Elemental analysis showed a Mg:butane ratio of 1.00:1.05. The nmr indicated the compound in benzene existed as an etherate complex: The benzene solution spectra showed a phenyl group multiplet at 7.98τ, a doublet at 8.38τ, a triplet at 8.72τ, and a multiplet at 9.88τ. The ethereal solution gave the following absorptions: A phenyl multiplet centered at 2.64τ, a multiplet at 8.31τ, a doublet at 8.62τ, a triplet at 9.02τ, and a multiplet at 9.65τ.

Preparation of n-butyl-sec-butylmagnesium

To a slurry of 0.5 moles of activated magnesium chloride (preparation described previously in this thesis under Preparation of Di-sec-butylmagnesium) in 100 ml of benzene was added 395 ml of a 1.27M solution of sec-butyllithium in hexane solvent. The mixture was stirred over a two hour period. Then 450 ml of a 1.11M solution of n-butyllithium was added and stirred over a 12 hour period. Analysis of the supernatent solution exhibited a Mg:butane ratio of 1.00:2.04. The solution was divided in half and each portion desolvated at 40° in vacuo. Diethyl ether was added to one portion and benzene to the other. Nmr spectra of each solution were obtained: The ether solution gave a multiplet at 7.18τ, a multiplet at 8.20τ, a doublet at 8.62τ, a triplet at 8.95τ, and a multiplet at 10.68τ. The benzene solution gave the following absorptions: a multiplet at 8.10τ, a multiplet

at 8.30τ, a multiplet at 8.45τ, a multiplet at 8.60τ, a multiplet at 8.80τ, and a multiplet at 9.80τ.

N-butyl-sec-butylmagnesium was also prepared by adding 100 ml of 1M di-sec-butylmagnesium in benzene to 100 mmoles of neat di-n-butylmagnesium and stirring for 24 hours. The completion of reaction was noted by disappearance of insoluble di-n-butylmagnesium.

Preparation of n-butyl-sec-butylmagnesium Triethylamine Complex

Five hundred ml. of a one molar n-butylmagnesium chloride triethylamine complex in benzene solvent was prepared according to the method developed by Ashby, et al.[6] To this solution was added 379 ml of a 1.32M sec-butyllithium solution in hexane. A white precipitate of lithium chloride formed immediately with the evolution of some heat. The solution was stirred over a 24 hour period and then filtered. Analysis of the solution gave a Mg:butane ratio of 1.00:2.00.

Hydrogenolysis of Dialkylmagnesium Compounds

Hydrogenolysis of Di-sec-butylmagnesium in Diethyl Ether

Fifty ml of a one molar di-sec-butylmagnesium diethyl ethereal solution was hydrogenolyzed at 3000 psi and 50° for a two hour period. Examination of the solution at this time showed that a small amount of white precipitate had formed. Analysis of the solid showed a Mg:H ratio of 1.00:1.97. Analysis of the solution showed a Mg:butane ratio of 1.00:2.01. After filtration this same solution was hydrogenolyzed for an additional two hour period using the conditions stated previously. At the end of this reaction time, the solution contained a large

amount of white precipitate. Analysis of the solution revealed that the solution was 0.68M in magnesium and the butane:Mg ratio was 2.01:1.00. The solid exhibited a Mg:H ratio of 1.00:1.98. The supernatent solution was again hydrogenolyzed for another two hour period using previous conditions. At the end of this reaction time the solution was filtered and analyzed. The analysis of the filtrate showed no magnesium or active butyl groups to be present. The solid exhibited a Mg:H ratio of 1.00:2.01.

Hydrogenolysis of Di-sec-butylmagnesium in Benzene

Fifty ml of a one molar solution of di-sec-butylmagnesium in benzene was hydrogenolyzed at 3000 psi and 50^{o} for a two hour period. At the end of this reaction time a small amount of white precipitate was noted. Analysis of the solid showed a Mg:H ratio of 1.00:1.94. Analysis of the solution showed a Mg:butane ratio of 1.00:1.98. The solution was hydrogenolyzed for an additional two hour period. A large amount of precipitate was noted after this reaction period. Analysis of the solution gave the following results: Mg = 0.54 molar; Mg:butane ratio = 1.00:2.05. The solid gave the following Mg:H ratio; 1.00:2.02. The supernatent solution was hydrogenolyzed for another two hour period. After filtration, analysis of the solution indicated no magnesium or active butyl groups present. Analysis of the solid gave the following: $Mg_{1.00}$, $H_{2.03}$. An Infrared spectrum was taken of the solid. Broad absorption from 800 cm^{-1} to 540 cm^{-1} was observed.

Hydrogenolysis of n-butyl-sec-butylmagnesium in Diethyl Ether

One hundred ml. of a one molar n-butyl-sec-butylmagnesium ethereal

solution was hydrogenolyzed for a four hour period at 3000 psi and 50°. Examination of the solution showed a minute amount of white precipitate present that could not be recovered. Analysis of the supernatent liquid gave a Mg:butane:H ratio of 1.00:1.82:0.19. The supernatent liquid was then hydrogenolyzed under the same conditions for an additional one hour period. A minute amount of white precipitate was present but again could not be recovered. Analysis of the supernatent solution gave the following: Mg:butane:H = 1.00:1.51:0.52. The supernatent solution was hydrogenolyzed for another one hour period under the same conditions as previously stated. At the end of this reaction time, a large amount of white precipitate was noted. After filtration analysis of the solid product gave a Mg:H ratio of 1.00:2.02.

An nmr spectrum of the supernatent solution at the end of a five hour period of hydrogenolysis at 3000 psi and 50° showed that the sec-butyl group absorbance had diminished. No new absorbance was noted. The nmr spectrum of the supernatent at the end of a six hour period of hydrogenolysis at 3000 psi and 50° indicated that the sec-butyl group was absent, however the n-butyl group absorbance was present. No new absorbances were noted.

A new 100 ml solution of n-butyl-sec-butylmagnesium (1.0 molar) was hydrogenolyzed for two hours at 80° and 3000 psi. A large amount of precipitate was found to be present at the end of the reaction time. Analysis of the supernatent solution gave the following: Mg:butane = 1.00:2.06. Analysis of the solid gave the following: Mg:H = 1.00:1.92. Nmr analysis of the solution revealed the absence of sec-butyl groups.

Hydrogenolysis of n-butyl-sec-butylmagnesium in Benzene

One hundred ml of a one molar solution of n-butyl-sec-butylmagnesium in benzene was hydrogenolyzed at 3000 psi and 50° for a four hour period. The solution contained a minute amount of white precipitate which was not recoverable. After filtration the solution gave the following analysis: Mg:butane:H = 1.00:1.78:0.25. The supernatent solution was hydrogenolyzed again for a one hour period under the conditions previously stated. This solution also contained an unrecoverable amount of white precipitate. Analysis of the supernatent solution gave the following: Mg:butane:H = 1.00:1.48:0.56. Hydrogenolysis of the supernatent solution for an additional hour under the conditions previously stated produced a solution which contained a large amount of white precipitate. After filtration the solution analysis was: Mg:butane = 1.00:1.94 and the solid analysis was: Mg:H = 1.00:2.02. The nmr spectrum of the solution after a five hour reaction period at 50° and 3000 psi showed the intensity of the sec-butyl group diminished. The nmr spectrum of the solution after a six hour period of hydrogenolysis at 50° and 3000 psi showed the absence of the sec-butyl group. No new absorbance was observed in either nmr spectrum.

A new 100 ml portion of a one molar solution of n-butyl-sec-butyl-magnesium in benzene was hydrogenolyzed at 80° and 3000 psi for a two hour period. A large amount of white precipitate was formed. After filtration the solution analysis was: Mg:butane = 1.00:2.04. The solid analysis gave the following results: Mg:H = 1.00:1.98. The nmr spectrum of the solution showed the absence of a sec-butyl group.

Hydrogenolysis of Phenyl-sec-butylmagnesium in Diethyl Ether

One hundred ml of a one molar ethereal solution of phenyl-sec-butylmagnesium was hydrogenolyzed for a five hour period at 50° and 3000 psi. An unrecoverable amount of white precipitate was present. Analysis of the supernatent solution after solvent removal gave the following analysis: benzene:Mg: butane:H = 1.00:1.00:0.50:0.50. The nmr spectrum of the solution showed a decrease in the intensity of the absorbance of the sec-butyl group and no new absorbance was observed. Hydrogenolysis of the solution for another one hour period at 50° and 3000 psi produced a large amount of white precipitate. Filtration and subsequent analysis of the filtrate gave the following: Mg:benzene = 1.00:1.90. Analysis of the residue gave the following analysis: Mg:H = 1.00:1.96. The nmr spectrum of this solution showed the absence of the sec-butyl group.

Hydrogenolysis of Phenyl-sec-butylmagnesium Etherate in Benzene

One hundred ml. of a one molar solution of phenyl-sec-butylmagnesium etherate in benzene was hydrogenolyzed at 50° and 3000 psi for a five hour period. An unrecoverable amount of white precipitate was present. Analysis of the filtrate gave the following: Mg:butane:H = 1.00:0.52:0.47. The nmr spectrum of the solution showed the phenyl group to be present in undiminished intensity, and the sec-butyl group to be present in diminished intensity. No new absorbances were observed. Continued hydrogenolysis of the solution for another one hour period under the same conditions shown above produced a large amount of precipitate in the solution. Analysis of the solution showed no butane present and the nmr spectrum showed the absence of the sec-butyl group. The filtered solid gave the

following: Mg:H = 1.00:2.02.

Hydrogenolysis of a Methyl-sec-butylmagnesium in Diethyl Ether

One hundred ml of a one molar ethereal solution of methyl-sec-butylmagnesium was hydrogenolyzed at 50° and 3000 psi for a five hour period. An unrecoverable amount of a white precipitate was present in the solution. Subsequent analysis of the supernatent liquid gave the following result: methane:Mg: butane:H = 1.00:1.00:0.55:0.51. (In analysis the methane and hydrogen could not be separated and their combined ratios was [H + Me] = 1.51). The nmr spectrum showed a ratio of sec-Bu to Me of approximately 0.5:1. No new absorbances were observed. Hydrogenolysis of the solution for another one hour period at 50° and 3000 psi produced a large amount of white precipitate which was analyzed after filtration and gave the following results: Mg:H = 1.00:2.03. The nmr spectrum of the solution showed the presence of only methyl groups and no sec-butyl group. No new absorbance was observed. The analysis of the solution gave the following results: Mg:methane = 1.00:2.01.

Hydrogenolysis of Methyl-sec-butylmagnesium Etherate in Benzene

One hundred ml of a one molar methyl-sec-butylmagnesium etherate in benzene solvent was hydrogenolyzed at 50° and 3000 psi for a five hour period. An unrecoverable amount of a white precipitate was present in the solution. Analysis of the solution gave the following results: methane: Mg:butane:H = 1.00:1.00:0.53:0.52. (As in the previous hydrogenolysis of this compound in ether solvent, the methane and hydrogen could not be separated and actual analysis was [H + Me] = 1.52. The nmr spectrum of the solution indicated a methyl

to sec-butyl ratio of 1:0.5). No new absorbances were observed by nmr. Hydrogenolysis of the solution for another one hour period at 50° and 3000 psi produced a large amount of white precipitate which was analyzed after filtration and gave the following result: Mg:H = 1.00:1.96. The supernatent solution was analyzed and gave the following results: Mg:methane = 1.00:2.01. The nmr spectrum revealed no sec-butyl group present, however a higher type of methyl group was present in the solution. No new nmr absorbances were observed.

Hydrogenolysis of the Triethylamine Complex of n-Butyl-sec-Butylmagnesium in Benzene Solvent

One hundred ml of a one molar solution of the triethylamine complex of n-butyl-sec-butylmagnesium in benzene was hydrogenolyzed at 50° and 3000 psi for a five hour period. The resulting solution was slightly cloudy. When filtered no residue was recovered but the solution was clear. The analysis of the solution gave the following: Mg:butane:H = 1.00:1.00:0.97. However, the solution became cloudy after one-half hour and precipitation of a white solid commenced. The precipitate was analyzed and gave the following results: Mg:H = 1.00:2.05. The solution analyzed after a 24 hour period, gave the following results: Mg:butane:H = 1.00:2.20:0.0.

Molecular Weight Determination of Partially Hydrogenated Dialkylmagnesium Compounds

If it is assumed that a single compound exists as solute in the partially hydrogenated solutions of mixed dialkyl (ayrl) magnesium compounds, the analytical

data suggest simplest formulas of the type ($RMgH \cdot R'MgR$). On the basis of this assumption, molecular weights were determined in both diethyl ether and benzene solvents. Molecular weight determinations in diethyl ether were performed ebullioscopically by a method developed by F. W. Walker and E. C. Ashby.[7] Molecular weight determinations in benzene were determined by freezing point depression. Tables of the data obtained are contained in the Appendix.

Low Temperature Nmr Profile of Methyl-sec-Butylmagnesium-Methyl Magnesium Hydride Complex in Diethyl Ether

Spectra of a 0.30M solution of partially hydrogenated methyl-sec-butylmagnesium ($s\text{-}C_4H_9MgCH_3 \cdot CH_3MgH$) in diethyl ether were recorded successively from room temperature to -80°. At room temperature a single sharp peak for the methyl group was observed at 11.30τ. At 0° the intensity of the methyl peak was slightly less than at room temperature and the position of the peak had shifted to 11.37τ. As the temperature was lowered to -20° the methyl signal shifted to 11.39τ and the intensity of the signal was slightly broadened. At -40° the methyl signal shifted to 11.41τ and broadened. At -60° the methyl signal became quite broad and asymmetric in shape and it centered at approximately 11.45τ. At -80° the methyl signal had been resolved into two asymmetric peaks of equal intensity. One signal was located at 11.15τ and the other signal at 11.68τ. At lower temperatures the complex began to precipitate.

CHAPTER III

DISCUSSION AND RESULTS

Redistribution Reactions

Magnesium hydride produced from the reaction of lithium aluminum hydride with diethylmagnesium [reaction (1)] was stirred over a 24 hour period with di-sec-butylmagnesium in the hope that redistribution would take place [reaction (2)].

$$(1)\quad 2\ Et_2Mg + LiAlH_4 \rightarrow 2\ MgH_2\downarrow + LiAlEt_4$$

$$(2)\quad MgH_2 + (sec\text{-}Bu)_2Mg \rightarrow sec\text{-}BuMgH$$

Analysis of the solution revealed however that redistribution failed to take place and the reactants were recovered.

Although magnesium hydride produced from lithium aluminum hydride is contaminated with some aluminum, it was thought that a catalytic amount of triethylaluminum might induce redistribution. Again redistribution failed to take place in diethyl ether or benzene.

The redistribution reaction was repeated using magnesium hydride obtained by hydrogenolysis of di-sec-butylmagnesium [reaction (3)].

$$(3)\quad (sec\text{-}Bu)_2Mg \xrightarrow[\text{3000 psi, } 50^{\circ}\text{, 8 hours}]{H_2} MgH_2\downarrow + 2\ C_4H_{10}$$

This source of magnesium hydride was used in the hope that a purer and more reactive form of MgH_2 might be more successful in the redistribution reaction. However, the analysis of the resulting solution and residue after a 24 hour period indicated that redistribution had failed to take place in diethyl ether or benzene.

A catalytic amount of triethylaluminum was again added to both the ethereal and the benzene redistribution reaction vessels. After a 24 hour stirring period analysis again indicated that redistribution had failed to take place in either solvent.

An ethereal solution of lithium aluminum hydride was stirred with neat di-sec-butylmagnesium in a molar ratio of 4:1 respectively. It was expected that the reaction would proceed according to the following equation:

$$(4)\quad LiAlH_4 + 4(sec\text{-}Bu)_2Mg \rightarrow LiAl(sec\text{-}Bu)_4 + 4\ sec\text{-}BuMgH$$

It was anticipated that both sec-butylmagnesium hydride and lithium tetra-sec-butylaluminate would be soluble in ether. The solution remained clear for about two hours, then a white precipitate began to form. The rate of precipitation increased with time. After 24 hours the precipitate and solution were analyzed. The precipitate was shown to be magnesium hydride. The solution analysis and infrared absorptions at 1805 cm^{-1}(Al-C stretch) and 522 cm^{-1} (Mg-C stretch) indicated LiAl sec-Bu_4 and $(sec\text{-}Bu)_2Mg$ were present. Therefore the actual reaction would appear to be the following:

$$(5)\quad LiAlH_4 + 4(sec\text{-}Bu)_2Mg \rightarrow 2MgH_2\downarrow + LiAl(sec\text{-}Bu)_4 + 2(sec\text{-}Bu)_2Mg$$

The reaction of di-sec-butylmagnesium and lithium aluminum hydride in

benzene solvent was initiated by adding 25 mmoles of neat lithium aluminum hydride to 100 mmoles of di-sec-butylmagnesium benzene solution. The expected reaction was as follows:

$$(6)\quad 4(\text{sec-Bu})_2\text{Mg} + \text{LiAlH}_4 \rightarrow \text{LiAl(sec-Bu)}_4 + 4\ \text{sec-BuMgH}$$

After a 24 hour stirring period the solution still contained a gray solid. Analysis of the solid and the solution indicated no reaction had occurred and the reactants were recovered unchanged.

Hydrogenolysis of Unsymmetrical Dialkyl Magnesium Compounds

Hydrogenolysis of di-sec-butylmagnesium in diethyl ether for any length of time produced only magnesium hydride. No hydrogenated alkyl-magnesium product was ever found in solution or in the precipitate. This would seem reasonable since little difference in the ease of cleaving the alkyl groups would be expected and also it is possible that if an RMgH compound were formed, it might redistribute to MgH_2 and MgR_2. The nature of the solvent seemed to have no effect on the reaction.

Hydrogenolysis of unsymmetrical dialkyl(aryl)magnesium ($RMgR'$) reagents was attempted using alkyl groups that are very different in ease of cleavage. The sec-butyl group can be removed under relatively mild conditions compared to a phenyl, methyl, or n-butyl group. So, the compounds used in the hydrogenolysis studies were sec-butyl-phenylmagnesium (PhMgsec-Bu), sec-butyl-methylmagnesium (MeMgsec-Bu), and sec-butyl-n-butylmagnesium (n-BuMgsec-Bu) which were expected

to produce PhMgH, MeMgH and n-BuMgH, respectively. The hydrogenolysis of all three compounds were carried out in both ether and benzene solvent.

Hydrogenolysis of all three compounds for less than about five hours only produced a minute white precipitate (slightly cloudy solution) that could not be recovered for analysis. This white precipitate was probably magnesium hydride. Hydrogenolysis for more than five hours resulted in a symmetrical dialkyl magnesium compound and magnesium hydride. Hydrogenolysis for five hours resulted in a partially hydrogenated soluble product. The following equations describe conditions and products of hydrogenolysis. In the following equations R = Ph, n-Bu, or Me.

$$(7)\quad \text{RMgsec-Bu} \xrightarrow[<5 \text{ hours, } 50^{\circ}, \text{ 3000 psi}]{\text{Benzene or Ether}} \text{N.R. (cloudy solution).}$$

$$(8)\quad 2\ \text{RMgsec-Bu} \xrightarrow[5 \text{ hours, } 50^{\circ}, \text{ 3000 psi}]{\text{Benzene or Ether}} \text{"RMgsec-Bu}\cdot\text{RMgH"}$$

$$(9)\quad 2\ \text{RMgsec-Bu} \xrightarrow[>5 \text{ hours, } 50^{\circ}, \text{ 3000 psi}]{\text{Benzene or Ether}} R_2Mg + MgH_2$$

The hydrogenolysis of the trimethylamine complex of n-butyl-sec-butylmagnesium produced the desired product (n-BuMgH$\cdot NEt_3$) or at least a tertiary amine solvate of the desired product. However this product disproportionated quickly on standing. It is believed that a more bulky amine such as tetramethylethylenediamine (TMEDA) might stabilize the product for a longer period of time; however, this approach should be the subject of a separate investigation.

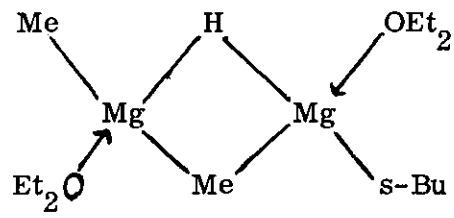
Molecular Association

Kamienski[1] as previously stated in Chapter I postulated the existence of partially hydrogenated dialkylmagnesium compounds and suggested that these compounds probably exist as dimers or trimers. Molecular association studies of partially hydrogenated solutions of RMgsec-Bu, were carried out by boiling point elevation in diethyl ether and by freezing point depression in benzene. The analytical data from these solutions showed approximately the following ratios: R:Mg:butane:H = 1.00:1.00:0.5:0.5.

The results of the molecular association studies are given in the tables in the Appendix. Although the simplest formula of the assumed compound is RMgH·RMgR′, it is more convenient to choose as the "formula weight of solute" the weight corresponding to one mole of Mg atoms. Then the experimentally determined association factor, i, gives the number of Mg atom in the molecule. Results of the molecular association studies indicate that all the products are dimers, i.e., contain two Mg atoms, whether in ether or benzene.

A low temperature 100 MHz nmr profile of MeMgsec-Bu·MeMgH in diethyl ether was carried out in order to support the dimer structure indicated by the molecular association studies. At room temperature the methyl group attached to magnesium was observed as a sharp singlet. As the temperature was lowered the peak broadened and shifted to a higher τ value. (From 11.30τ at room temperature to 11.41τ at -60^{o}). At -80^{o} the methyl signal resolved into two peaks of equal intensity, one at 11.15 and one at 11.68. The two signals for the methyl group are indicative of two different environments for the methyl group. The lower field signal is attributed to

the bridging methyl group and the higher field signal is attributed to the terminal methyl group as shown below.



Based on the fact that molecular association studies indicate that the partially hydrogenated complex is a dimer and nmr studies indicate a terminal and bridging methyl group of equal intensity, the above structure seems reasonable. The ether is coordinated to the magnesium in benzene solvent as well as in ether solvent since the complex exists as an etherate in benzene.

CHAPTER IV

CONCLUSIONS

It is clear that alkylmagnesium hydrides disproportionate to magnesium hydride and dialkylmagnesium compounds regardless of the method of preparation or solvent used. Some stability toward disproportionation was observed when the RMgH compound was complexed to a tertiary amine. It is suggested that this stabilization would be an interesting problem for a future investigation.

Partial hydrogenation of unsymmetrical dialkylmagnesium compounds ($RMgR'$) where R = Ph, Me and n-Bu and R′ = sec-Bu, produced compounds of empirical formula $RMgH \cdot RMgR'$ which were shown by both molecular association and low temperature nmr studies to exist as a stable mixed hydrogen-methyl bridge compound in solution.

APPENDIX

Equations Used in Molecular Weight Determinations of Partially Hydrogenolyzed Dialkyl (Aryl) Complexes

Equation (1)

The following equation was used in determining molecular weights of partially hydrogenolyzed $RMgR'$ compounds in ether solvent by boiling point elevation.[7]

$$i = \frac{M_2}{M_1}$$

$$M_2 = \frac{(1000K_B)(W_1)}{(\Delta T_B)(W_2)}$$

Term Definitions:

W_1 = Weight of solute.

W_2 = Weight of solvent.

M_1 = Formula weight of solute.

M_2 = Experimentally determined weight of solute.

K_B = Boiling point elevation constant (2.01 for diethyl ether at 740 mm of pressure).

ΔT_B = Boiling point elevation.

i = Experimentally determined molecular weight of solute divided by the formula weight of the solute.

Equation (2)

The following equation was used in determining molecular association of

partially hydrogenolyzed RMgR′ compounds in benzene solvent by freezing point depression.

$$i = \frac{M_2}{M_1}$$

$$M_2 = \frac{(1000K_F)(W_1)}{(\Delta T_F)(W_2)}$$

Where:

Term Definitions:

W_1 = Weight of solute.

W_2 = Weight of solvent.

M_1 = Formula weight of solute.

M_2 = Experimentally determined weight of solute.

K_f = Freezing point depression constant for benzene (4.9).

ΔT_f = Freezing point depression.

i = Experimentally determined molecular weight of solute divided by formula weight of solute.

Formula Weights of Solute

The formula weight of the solute was calculated by the following:

1/2 Formula Weight of (RMgR′·RMgH)

Complex	Formula Weight	1/2 Formula Weight
PhMgsec-Bu·PhMgH	260.78	130.39
MeMgsec-Bu·MeMgH	136.74	68.37
n-BuMgsec-Bu·n-BuMgH	220.86	110.43

Table 1. Molecular Association Data of PhMgsec-Bu·PhMgH, MeMgsec-Bu·MeMgH, and n-BuMgsec-Bu·n-BuMgH in Diethyl Ether

Fraction	W_1	W_2	ΔT_B	Molality	i
		"PhMgsec-Bu·PhMgH"			
1	0.568	33.23	0.139	0.131	1.89
2	0.772	34.86	0.171	0.170	1.99
3	0.977	35.29	0.213	0.212	1.99
		"n-BuMgsec-Bu·n-BuMgH"			
1	0.482	37.45	0.117	0.117	2.00
2	0.759	39.98	0.181	0.171	1.90
3	1.034	42.53	0.226	0.220	1.95
		"MeMgsec-Bu·MeMgH"			
1	0.276	39.242	0.109	0.103	1.88
2	0.546	39.542	0.203	0.202	1.99
3	0.832	39.908	0.305	0.305	1.99

Table 2. Molecular Association Data of PhMgsec-Bu·PhMgH, MeMgsec-Bu·MeMgH, and n-BuMgsec-Bu·n-BuMgH in Benzene

Fraction	W_1	W_2	ΔT_F	Molality	i
		"PhMgsec-Bu·PhMgH"			
1	0.357	34.74	0.198	0.08	1.95
2	0.572	42.22	0.268	0.104	1.90
3	0.798	49.00	0.298	0.125	2.05
		"n-BuMgsec-Bu·n-BuMgH"			
1	0.667	65.30	0.220	0.09	2.06
2	0.918	71.80	0.269	0.116	2.11
3	1.169	77.30	0.335	0.137	2.00
		"MeMgsec-Bu·MeMgH"			
1	0.177	57.16	0.129	0.045	1.71
2	0.360	61.37	0.215	0.086	1.96
3	0.555	65.70	0.283	0.124	2.15

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